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(54) **Method of removing scale.**

(57) Scale is removed from a metal article by agitating against the article solid bodies wetted by an aqueous acidic scale removing composition. The composition preferably has a temperature above ambient and is an aqueous acidic solution of a chelating agent.

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METHOD OF REMOVING SCALE

Numerous methods are known for cleaning an article and generally involve abrasion or washing or a combination thereof. Effective washing is often achieved using an aqueous alkali solution. Contact between the solution and the article can be achieved simply by immersing the article in the solution or by various other methods, for instance by sprays, jets or brushing. One of the numerous ways of effecting contact that has been proposed involves barrelling, tumbling or vibrating the article in a wetted medium of small stones or ceramic, metal or plastic shapes that may contain embedded abrasive. Unfortunately these methods tend to be totally incapable of removing the scale that may form on refractory alloys during heating.

If heat resistant and corrosion resistant ferrous or non-ferrous refractory alloys, for example 18/8 nickel-chromium stainless steels and nickel-cobalt base creep-resistant alloys, are subjected to heat treatment or are used under conditions of high temperature an oxide scale is often formed on them. It is usually necessary to remove this scale in order to facilitate subsequent operation such as welding, brazing, close fitting assembly or size or defect inspection processes. A particular problem arises with jet engine turbine blades, for instance formed of nickel-cobalt based alloys, since scale tends to form on them during use and must be removed from time to time. Known methods of scale removal include mechanical methods and chemical

methods.

Known mechanical scale removal methods include shot blasting, abrasive grit blasting, blasting with aqueous abrasive suspensions, grinding, linishing and buffing. These methods are time-consuming, labour-intensive and incur metal loss.

Various chemical methods are known. One method involves contacting the article with neutral or alkaline molten salts, the latter often in the presence of sodium hydride. Such methods tend sometimes to be ineffective and are dangerous to operate.

Another method involves pickling the article in an acid solution generally containing an inhibitor. The method may be supplemented with alternating treatments in an aqueous alkaline oxidising bath such as a caustic/permanganate composition. These methods also are not very satisfactory, and in particular they tend to be ineffective in removing scale from heat resisting alloys and they may lead to metallurgical defects such as intergranular attack.

Other chemical methods involve contacting the article with an acidic chelating solution, again optionally being alternated with an alkaline oxidising bath. However it is often found that it is difficult or impossible to remove all the scale by such solutions, especially when the scale has formed over a long period of time on refractory alloys, with the result that contact between the solution and the article has to be maintained for many hours.

The difficulty of removing scale is so acute that some operators are finding it necessary, despite the attendant disadvantages, to abandon the use of chemical treatments and revert instead to the mechanical methods discussed above.

Contact between the solution and the article traditionally is by simple immersion but more sophisticated methods are also known. For instance in British Patent Specification No. 1475307 apparatus is described

by which the contact can be achieved by a combination of pressure jets and acoustic vibration. The fluid used may consist solely of liquid or may involve particulate solid material dispersed in the liquid. Unfortunately this process requires expensive and complex apparatus and is not easily operated for careful scale removal.

A difficulty with many methods of scale removal is that there is a tendency for the method either to result in incomplete removal of scale or to result in the removal of substantial amounts of the metal substrate. It has been our object to devise a method that is capable of giving very efficient removal of scale with minimum removal of metal.

In the invention scale on a metal article is removed by contact of the article in a vessel with an aqueous acidic scale removing composition, and in this method the vessel contains solid bodies wetted by the composition and the contact of the article with the solution is effected by agitating the wetted bodies against the article.

The bodies generally have dimensions of between 0.2 and 20 mm. There are voids between the bodies in the vessel and the amount of composition in the vessel is insufficient to fill the voids. Thus the amount should be less than the amount required to form a continuous phase in which the bodies could be suspended. Preferably the amount of composition is less than 75%, and preferably less than 50%, of the volume required to fill the voids. However the volume of composition must be sufficient to wet all the bodies in the vessel and may be, for instance, at least 10% of the volume required to fill all the voids. By using an amount of composition that is insufficient to fill all the voids the scale removal is much more effective than if the vessel were filled with the composition.

As a result of promoting contact of the

specified composition by the specified method of agitation we surprisingly find that it is possible to obtain a marked acceleration in the rate of scale removal and/or that scale can be removed from workpieces which cannot effectively be treated by simple immersion in the composition, and yet this scale removal can be achieved in a controlled manner such that there is little or no removal of metal. It is very surprising that this successful result can be achieved since the method seems to be primarily chemical and yet the improved results are obtained using less composition than is required in traditional immersion methods.

It can be demonstrated that the effect is not simply abrasion caused by the solid bodies, since it has been found that, if the aqueous acidic composition is replaced by water or a conventional cleaning solution, e.g. of sodium silicate, there is little or no scale removal.

The solid bodies may be made of, for example, ceramic, refractory, abrasive or metallic. The bodies may be any suitable shape and size. They may be spherical but preferably are polyhedral, having a small number of faces, e.g. up to eight. Thus, for example, the bodies may be right triangular prisms or cubes. Alternatively, the bodies may be obtained by crushing a block of a suitable material, e.g. fused alumina. The minimum dimension of the bodies is preferably at least 0.5, and usually at least 2 mm. The maximum dimension may be no more than 20, 10 or even 6 mm. The agitation may involve barrelling or tumbling but preferably the vessel is a trough containing a bed of the bodies, the article is submerged in the bed and the bodies are agitated by agitating the trough. For instance the trough may be vibrated and if the trough is circular, or, more preferably, spiral or annular shaped it may be vibrated with a rotational motion. Suitable apparatus for use in the method is known and is readily available under the trade name "Spiratron" which is

manufactured by Cetema Limited of School Lane, Knowsley Industrial Estate, Prescot, Merseyside, England.

The composition is preferably above ambient temperature during the process, suitably at a temperature of 40 to 100°C, e.g. about 80°C. For this purpose it is necessary to adapt the apparatus specially in order to permit the maintenance of the desired temperature during use. Preferably the composition is heated outside the vessel by a heater, is circulated through the vessel for contact with the article, and is recycled to the heater, where it is reheated and then circulated through the vessel again. Accordingly the composition may be continuously trickled into the vessel from a heater, continuously removed from the vessel and recycled to the heater.

The total treatment of the article may involve alternation of the described method with contact with an oxidising alkaline solution. Thus the method may comprise contacting the article with the said wetted and agitated bodies in the vessel, removing the article from the vessel, contacting the article with an oxidising alkaline solution and then repeating the contact of the article in the vessel with the wetted and agitated bodies. The alkaline oxidising solution typically contains sodium hydroxide and potassium permanganate and is usually hot, e.g. 95°C. Generally it is a static solution and contact is achieved by immersing the article in the solution. Generally the article is rinsed between each treatment.

The invention is of particular value when the scale removing composition is an acidic solution of a chelating agent, often a solution of an acidic chelating agent. Suitable chelating agents are tartaric acid, citric acid, ethylenediaminetetraacetic acid and nitrilotriacetic acid. The composition should be mildly acid and so will usually have a pH of at least 2, e.g. from 2.5 to 6. It may include components additional to the chelating agent and any

necessary acid to generate the chosen pH, for instance reducing agents, surfactants and corrosion inhibitors. Broadly, chelating compositions known for scale removal of refractory oxides can be used in the invention but the method of the invention results in very much more effective scale removal than has previously been attainable. Thus as a result of the invention it is no longer necessary to revert to mechanical methods such as abrasive grit blasting in order to achieve good scale removal. The invention is of particular value when the described acidic chelating compositions are used in the described method for the removal of scale from nickel-cobalt based alloys, for example turbine blades from jet engines.

The following example illustrates the invention. Used cobalt-nickel turbine blades from a J79 jet engine were treated in a Spiratron using, as medium, 6 mm ceramic triangular prisms irrigated with a hot chelating solution of ethylene diamine tetra-acetic acid and a surfactant and having a pH of 3.5 to 4.0. The vibrating mass was maintained at a temperature of approximately 75°C. During the process the chelating solution was constantly being heated, trickled through the vibrating mass, withdrawn from the mass and reheated.

After two hours treatment, the parts were removed, rinsed, and immersed for ½ hour in a solution containing 8% potassium permanganate and 15% sodium hydroxide maintained at 95°C. Following rinsing, a further two hours treatment in the bodies wetted with the chelating solution resulted in a complete removal of scale from the blades, which presented a semi-polished appearance.

The weight loss of scale from the blade amounted to approximately 550 mg. Further weight loss from the cleaned blade in the agitated hot wetted medium was at the rate of approximately 5 mg per hour. Using a solution of sodium silicate for 10 hours in the same vibrated medium produced no apparent cleaning effect.

Cleaning similar blades but without agitation

required a total immersion time of approximately 7 hours.

A suitable solution for use as the chelating solution defined in this example is the material sold commercially by Ardrox Limited, of Furlong Road, Bourne End, Buckinghamshire, England as their product Ardrox 1871. "Ardrox" is a trade mark.

CLAIMS

1. A method in which scale on a metal article is removed by contact in a vessel with an aqueous acidic scale removing composition characterised in that the vessel contains solid bodies wetted by the composition and the contact of the article with the solution is effected by agitating the wetted bodies against the article.

2. A method according to claim 1 characterised in that the bodies have dimensions of between 0.2 and 20 mm, there are voids between the bodies and the amount of composition in the vessel is insufficient to fill the voids.

3. A method according to claim 1 or claim 2 characterised in that the composition is at a temperature above ambient temperature.

4. A method according to claim 3 characterised in that the composition is heated outside the vessel by a heater, circulated through the vessel for contact with the article and recycled to the heater.

5. A method according to any preceding claim characterised in that the vessel is a trough containing a bed of the bodies and the article is submerged in the bed and the bodies are agitated by agitating the trough.

6. A method according to any preceding claim characterised in that the article is contacted with the said wetted and agitated bodies in the vessel, the article is then removed from the vessel and is contacted

with an oxidising alkaline solution, and the article is then contacted in the vessel with the said wetted and agitated bodies.

7. A method according to any preceding claim characterised in that the scale removing composition is an acidic solution of a chelating agent.

8. A method according to claim 7 characterised in that the solution has a pH of from 2 to 6 and includes one or more additives selected from reducing agents, surfactants and corrosion inhibitors.

9. A method according to claim 7 or claim 8 characterised in that the composition has a temperature of 40 to 100°C.

10. A method according to claim 7, claim 8 or claim 9 in which the article is a nickel-cobalt based alloy.

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EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X	FR-A-2 000 555 (CELANESE CORP) *Claims 1-5; page 5, line 17 to page 6, line 2*	1-3,6	C 23 G 1/02 B 24 B 31/14
A	FR-A-1 550 769 (JOHNS MANSVILLE)		
A	FR-A-2 153 628 (OXY METAL FINISHING)		
A	FR-A-1 423 822 (E.J.MICHEL)		

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 23 G 1/00
G 23 G 1/02
B 24 B 31/14
B 01 J 19/06
C 23 F 1/00
C 23 G 5/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25-06-1982	TORFS F.M.G.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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